Improving Measurements with NIST's Ozone Reference Standard

The concentration of ozone in the atmosphere continues to be an important global issue both scientifically and politically. Stratospheric ozone protects the Earth from harmful ultraviolet radiation, while tropospheric ozone is a major health concern and contributes to global climate change as a greenhouse gas. The NIST Standard Reference Photometer (SRP), developed jointly with the U.S. Environmental Protection Agency (U.S. EPA), has provided an infrastructure for the calibration and traceability of ozone measurements within the U.S. since 1983. NIST has also provided SRPs to 19 international laboratories in 16 countries including several SRPs to the International Bureau of Weights and Measures (BIPM) to serve as an ozone reference standard under the International Committee of Weights and Measures (CIPM).

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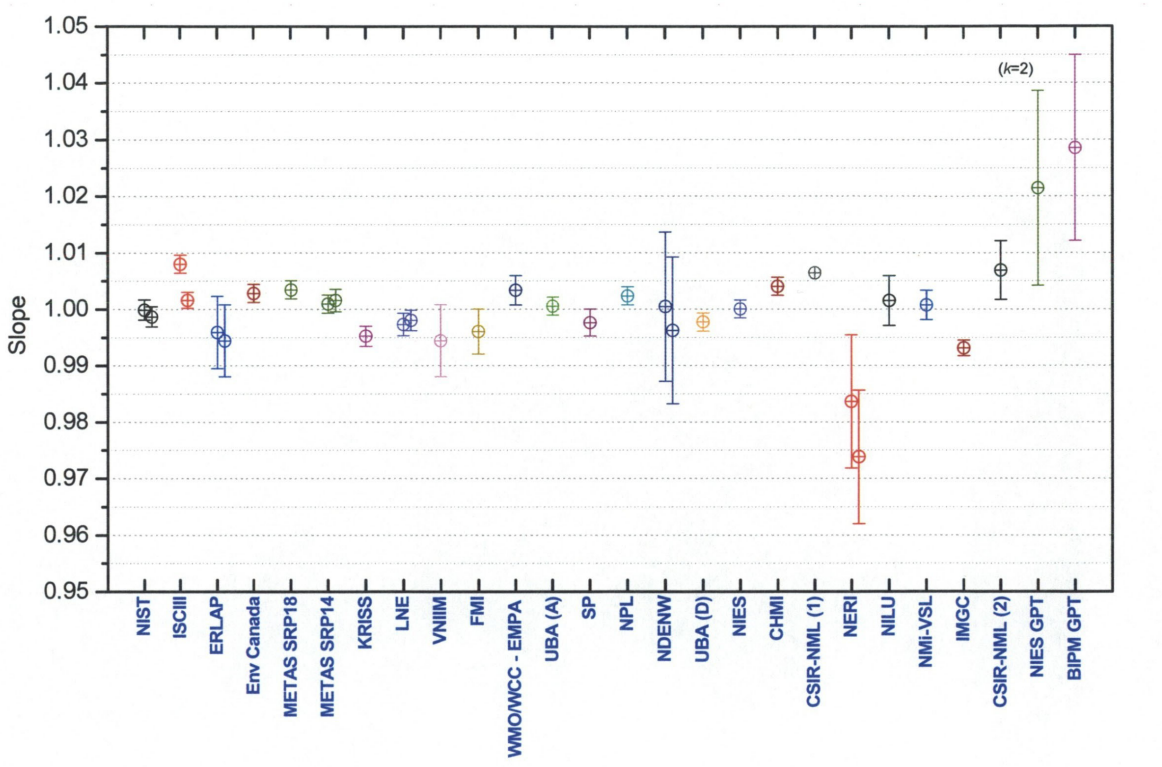
In 2005, the BIPM completed a pilot study on ozone comparability (CCQM-P28) in which 23 laboratories participated. Of the 23 laboratories, 11 maintain a NIST SRP and several others utilize SRP traceability. A recent in-depth study by the BIPM of systematic bias in the SRP has revealed a temperature measurement bias causing an underestimate of ozone mole fractions by 0.4%, and an optical measurement bias causing an overestimate of ozone mole fractions by 0.5%. NIST is investigating instrument modifications to reduce or eliminate these biases.

In order to maintain the NIST SRP as a high-level ozone reference standard for the world, NIST must develop modifications to significantly reduce these measurement biases, and document the effects in measurement results. The plan is to reduce or eliminate a temperature gradient through the absorption cells caused by the transfer of heat from a heated source lamp block. This can be accomplished by a re-design of the heated source lamp block and associated mounting scheme to isolate the heat source from the cells. Additionally, the BIPM study found that there are multiple reflections inside the SRP absorption cells causing an underestimation of the actual cell length. The optical filters mounted just past the absorption cells and in front of the detectors are known to have high reflectivity and are also adding to the multiple reflections within the cells. The BIPM study found that using slight angles on the absorption cell windows effectively removes the inner reflectivity between them. New cells are currently being developed with each cell end having its window placed at 3° angles. These new cells will be tested with various optical filters and physical positioning to examine the effects and document the measurement results.

NIST is redesigning its Standard Reference Photometer to eliminate the systematic bias found in ozone measurement worldwide.



Major Accomplishments: During the past year, NIST has performed an SRP temperature study to show the effects of different temperature gradients on the measurement of ozone mole fractions, and to re-design the existing system to substantially reduce this temperature gradient. The study looked at comparisons of two SRPs leaving one unchanged and making changes to the other while measuring the temperature gradient along one absorption cell. The study was done within the SRP source lamp block operating temperature range of 50 °C to 60 °C. Additionally, the source lamp block cover was shown to affect the temperature gradient and was quantified. The study has shown the original design to have a temperature gradient of 1.1 °C, corresponding to an ozone mole fraction bias of 0.39 %. The ability to reduce the temperature gradient from 1.1 °C down below 0.1 °C was also demonstrated using a redesigned source lamp block and different mounting components.

NIST participated in the CCQM-P28 ozone, ambient level pilot study along with 10 other laboratories that maintain a NIST SRP as their national standard. The study revealed overall agreement of SRPs to 0.7%, which is consistent with the original SRP comparisons done at NIST. It is believed that this measurement agreement can be improved once the SRP biases are reduced or eliminated. The graph shows the results of the slopes of all measurements performed in the CCQM-P28 study.

Impact: The worldwide interest in the NIST SRP to serve as a high-level national reference standard for ozone measurement and traceability has been increasing each year and is expected to continue. Proper maintenance and measurement comparability of all SRPs has a direct effect on global ozone measurements within the troposphere.

Future Plans: Upon completion of the study on the temperature and optical measurement biases in the SRP, an upgrade package will be made available to all existing SRPs, and will become part of any newly constructed SRP. Changes in the ozone mole fraction measurement with an SRP will be clearly quantified and documented. In 2006, NIST will participate in a CCQM key comparison on ozone at ambient levels.